

SYNTHETIC MIMICS FOR VISCOSITY AND SPECTRA OF H-COAL ASPHALTENES

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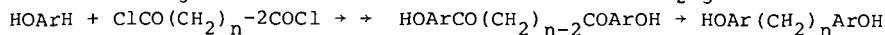
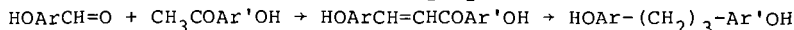
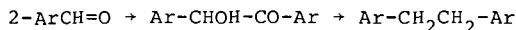
Asphaltenes from liquefaction of coal have characteristic properties of solubility, viscosity, and spectroscopy that on the one hand require explanation, and on the other hand could provide insight into the complex chemical nature of these substances. Knowing that asphaltenes can be separated into neutral, acidic and basic fractions and that the acids are phenolic and the bases are apparently pyridine derivatives, we turned our attention to the hypothesis that phenolic structures having two or more hydroxyl groups per molecule and heterocyclic bases of the pyridine type with two or more basic sites might when mixed display properties similar to those observed in asphaltenes.

In choosing model compounds, we noted that asphaltenes have nuclear magnetic resonance spectra showing some absorption in the region δ 3 to 4. This is too far upfield to be due to aromatic or olefinic hydrogens, and too far downfield to be due to simple alkyl groups, even when they bear phenyl substituents. However, the greater electron-withdrawing power of the pyridine ring might be enough to shift aliphatic resonance to that region. We therefore chose structures having two or more phenol or pyridine rings linked by a series of methylene groups ranging between one and six. Such compounds would be capable of multiple hydrogen bonding with each

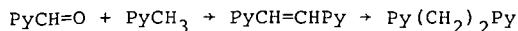


other, analogous to asphaltenes (1), and their mixtures could be anticipated to have high viscosities. Furthermore, we had already demonstrated the presence of chains of methylene groups in asphaltenes (2).

Methylene-4,4'-bisphenol and its 2,2'-isomer are commercially available. Bisphenols with a two-carbon bridge were synthesized from the appropriate benzaldehyde by the benzoin condensation and reduction. Bisphenols with other bridges were prepared as shown in the equations, utilizing the Fries rearrangement. Trisphenols were prepared by a double Fries rearrangement, and tetrakisphenols were prepared from bisphenol ethers by a double Friedel-Crafts reaction using methoxyphenylalkanoyl chlorides, reduction, and demethylation.



Bispyridines and bisquinolines were prepared as shown, or were prepared from quinolylmethylolithium and an α,ω -dibromoalkane.



1-(2-Pyridyl)-2-(2-hydroxyphenyl)ethane was prepared analogously from α -picoline and salicylaldehyde and reduction of the resulting stilbene analog with H_2/Pd .

The compounds and their properties are listed in Table I. The nmr spectra of the bispyridines, and especially the bisquinolines, simulate the aliphatic region of asphaltene spectra, including the downfield end, reasonably well.

Mixtures of a phenol and a pyridine from this group were more difficult to dissolve than the pure compounds, and tetrahydrofuran was the only inert solvent that showed a general ability to dissolve them. In this respect, there is a similarity to preasphaltenes of H-coal vacuum bottoms.

Table I
Phenols and Pyridines

No.	Compound	mp, °C	"aliphatic" ^a NMR, ppm
	4-HOC ₆ H ₄ (CH ₂) _n C ₆ H ₄ -OH		
1.	n = 2	198-99	2.9
2.	n = 3	96-98	1.6-2.8
3.	n = 4	158-59	1.5-2.5
	3-HOC ₆ H ₄ (CH ₂) _n C ₆ H ₄ -3-OH		
4.	n = 3	131-33	2.0, 2.8
	2-HOC ₆ H ₄ (CH ₂) _n C ₆ H ₄ -2-OH		
5.	n = 1	115-17	4.2
6.	n = 3	83-85	1.0-2.8, 5.3
	2-HO-5-CH ₃ C ₆ H ₃ (CH ₂) _n C ₆ H ₃ -5-CH ₃ -2-OH		
7.	n = 5	103-05	2.7, 4.8
8.	n = 6	123-24	1.4, 2.2
	C ₅ H ₄ N-2-(CH ₂) _n -2-C ₅ H ₄ N		
9.	n = 2	107-10	3.4
10.	n = 3	liq.	2.0-2.5, 2.6-3.1
	C ₅ H ₄ N-4-(CH ₂) _n -4-C ₅ H ₄ N		
11.	n = 2	109-109.5	2.95
12.	n = 3	57-60	1.9-2.4, 2.5-3.0
13.	C ₅ H ₄ N-2-(CH ₂) ₂ -4-C ₅ H ₄ N	liq.	2.95
14.	C ₅ H ₄ N-3-(CH ₂) ₂ -4-C ₅ H ₄ N	34-36	2.95
15.	C ₅ H ₄ N-2-(CH ₂) ₂ -3-C ₅ H ₄ N	liq.	2.90
	2-quinolylyl(CH ₂) _n -2-quinolylyl		
16.	n = 2	162-63	3.55
17.	n = 6	90-91.5	1.3-2.2, 2.9-3.3
18.	2-C ₅ H ₄ N-(CH ₂) ₂ -2-C ₆ H ₄ OH	87.5-88	3.18

a. In all compounds, aromatic ¹H resonance occurred in the region 7-9 ppm.

Initially, we planned to measure viscosity in solution, owing to the facts that most of the compounds were solids, and the quantities

were in most cases small, owing to the laborious syntheses. The solvents used by previous workers to study the effect of hydrogen bonding on viscosity (benzene, ethanol, ethyl or amyl acetate) would not dissolve sufficient quantities of our materials, and we were driven to use tetrahydrofuran. This solvent had already been used to study association in asphaltenes by Schwager, Lee and Yen (1), using vapor pressure osmometry.

Measurements of solutions of single phenols or pyridines and mixtures of them were made in 0.1 molar solutions in THF on an Ubbelohde viscometer at $25.00 \pm 0.02^\circ$, calibrated against water, dimethyl sulfoxide, and THF. The values of η so obtained are shown in Table II.

Table II
Viscosities of 0.1 M Solutions in Tetrahydrofuran

Solutes	θ (sec)	ρ (g/ml)	η (cp)
None			0.461
17	107.2	0.8930	0.5017
6	106.0	0.8909	0.4948
6 + 17	108.2	0.8952	0.5076
15	104.1	0.8880	0.4845
6 + 15	105.0	0.8906	0.4901
15 + methylene-2,2'-bisphenol	105.8	0.8896	0.4933

The results show that the viscosities, η , do not distinguish the solutions in which O-to-N hydrogen bonding can occur from those in which it cannot. This fact appears to arise from the nature of the solvent, which can itself act as an acceptor in hydrogen bonding. The energy of formation of the phenol-THF hydrogen bond has been reported to be 2.6 kcal/mol (3) and that of the phenol-pyridine hydrogen bond to be 8.0 kcal/mol (4). However, in the 0.1 M solutions, the concentration of the solvent THF is two orders of magnitude greater than that of the pyridine, such that the solvent can compete effectively with the pyridine for the phenol. This leveling effect greatly reduces the validity of studies of hydrogen bonding between substrates in THF; unfortunately, the solubility characteristics of the substrates did not allow a more inert solvent to be used.

The foregoing results demonstrated that viscosities would have to be measured on undiluted melts in order to investigate the role of hydrogen bonding. Such experiments require much larger samples than we had been able to prepare of most of the substrates, and we therefore limited these experiments to those substances that were available in sufficient quantity. Furthermore, the necessity to work with melts at elevated temperatures dictated a change in measurement technique, and we therefore used a Brookfield Engineering Laboratories model LVT rotational viscometer, using a Brookfield UL sample cell suitable for viscosities of 1 to 10 cp, or a specially designed small sample cell (1.5-2.0 ml) for viscosities in the range 100-10,000 cp. The entire apparatus was enclosed in a glass container which was immersed in a thermoregulated bath of silicone oil. Measurements on model compounds were made on 15-g. samples under an argon atmosphere at a series of increasing temperatures. Measurements were reproducible after cooling and remelting for the model compounds, but not for coal-derived materials until the sample had been subjected to several heating/cooling cycles.

Although a range of temperatures was used in each case, variations in melting point and viscosity precluded comparing all samples at the same temperature. Changes in shear rate (6, 30, 60 rpm) showed some non-Newtonian behavior (shear thinning), which was pronounced with some samples. Comparison of samples is thus more reliable at higher shear rates, and only values at 60 rpm are shown here. Representative results are given in Table III.

Table III
Viscosities of Undiluted Melts at 60 rpm and Activation Parameters
 $\ln \eta = A + E_{\eta}/RT$

Sample	at 160° (cp)	at 180° (cp)	at 210° (cp)	A	$E_{\eta} \frac{a}{\eta}$
11	1.25			-5.1	4.6
12	1.39			-5.2	4.9
CH ₂ (4-C ₆ H ₄ OH) ₂		3.99	2.70	-5.6	6.3
CH ₂ (2-C ₆ H ₄ OH) ₂	4.84	3.45	2.13	-6.2	6.7
CH ₂ (4-C ₆ H ₄ OH) ₂ + 11	6.55	4.19	2.26	-8.0	8.4
CH ₂ (2-C ₆ H ₄ OH) ₂ + 11		4.24	2.12	-10.0	10.4
CH ₂ (2-C ₆ H ₄ OH) ₂ + 12	3.58	2.45		-10.2	9.9
CH ₂ (4-C ₆ H ₄ OH) ₂ + 12			2.48	-4.8	5.6
2 + 11	5.17	3.68		-6.3	6.9
18	2.77	2.08		-8.1	7.8
"oils & resins" ^b	3.84	2.70		-7.5	7.6
"low mol. wt." asphaltenes ^c		6.95	4.68	-5.7	6.9
"high mol. wt." asphaltenes ^c			1550.0 ^d	-5.2	55.5

a. kcal/mol. b. Pentane-soluble fraction of H-coal vacuum bottoms.
c. See text. d. At 200°.

The measurements at different temperatures (a greater range and number of points than given in Table III) allow the activation energy for viscous flow, E_{η} , to be determined from the Eyring equation (5), $\ln \eta = A + E_{\eta}/RT$. These values are given in Table III, although this equation is of uncertain validity for molecules that are far from spherical (6). The linearity of a plot of $\ln \eta$ vs. $1/T$ may be used as a gauge of its applicability to a given system; the data for the various model systems were closely linear, with a correlation coefficient of 0.97-0.99. For coal-derived materials, the equation is less reliable (correlation coefficient 0.91-0.96), some curvature being noticeable at higher temperatures.

The activation energies are of the same order of magnitude as the energy of the hydrogen bond, except for the "high molecular weight" asphaltenes (soluble in toluene, but insoluble in 75% pentane/25% toluene), the value for which is more than five-fold those of the others, and in particular, is eight times as high as that for "low molecular weight" asphaltenes (soluble in 75% pentane/25% toluene).

Among the foregoing data, the system 2 + 11 provides a reasonably good simulation of the viscosity characteristics of "low molecular weight" asphaltenes. Both the activation parameters and the manifestation of non-Newtonian behavior vary with the length of the connecting chain of methylene groups and the position of the

H-bonding sites, and further study of the relationship may provide a more precise delineation of the structural possibilities for coal-derived liquids. It appears, however, even at this stage, that the "high molecular weight" asphaltenes owe their viscosity to a major extent to other causes.

We have made similar comparisons of the infrared spectra of melted asphaltenes and of model systems at elevated temperatures, using an electrically heated cell with internal temperature sensing, and recording the spectra over a range of temperatures. As was expected, the absorptions due to associated O-H decreased in comparison to unassociated O-H as the temperature was raised. The general form and the temperature sensitivity for asphaltenes and for mixtures of model phenols and pyridines were qualitatively similar.

REFERENCES

- (1) I. Schwager, W. Lee and T. Yen, Anal. Chem., **49** (14), 2323 (1977).
- (2) P. A. S. Smith, J. C. Romine and S.-S. P. Chou, Div. Petrol. Chem., Am. Chem. Soc., Preprints, **24**, 974 (Sept. 1979).
- (3) N. Nametkin, A. Kashevnik, M. Kurashev and T. Veretyakhina, J. Gen. Chem. (USSR), **47**, 2168 (1977).
- (4) R. Drago, G. Vogel and T. Needham, J. Am. Chem. Soc., **93**, 6014 (1971).
- (5) H. Eyring, J. Chem. Phys., **4**, 283 (1936).
- (6) S. Brush, Chem. Rev., **62**, 5131 (1962); S. Breitting and J. Magill, J. Appl. Phys., **45** (10), 4167 (1974).